NAVY DEPARTMENT
OFFICE OF NAVAL RESEARCH
WASHINGTON, D. C.

13 January 1954
Report No. 779
(Quarterly)
Copy No. 1

INVESTIGATION OF LIQUID ROCKET PROPELLANTS

★

Contract N7onr-462
Task Order No. III
Project No. NR 220 023

Aerojet-General CORPORATION
A SUBSIDIARY OF THE GENERAL TIRE & RUBBER COMPANY
AZUSA, CALIFORNIA

THE GENERAL TIRE

13 January 1954

Report No. 779
(Quarterly)

INVESTIGATION OF

LIQUID ROCKET PROPELLANTS

Contract N7onr-462
Task Order III
Project NR 220 023

Written by:

A. F. Graefe
R. E. Meyer
K. H. Mueller
E. M. Wilson

Approved by:

C. L. Randolph
Senior Chemist
Solid Engine and
Chemical Division

No. of Pages: 19

Period Covered:

1 September through 30 November 1953

Approved by:

D. L. Armstrong
Principal Chemist
Solid Engine and
Chemical Division

AEROJET-GENERAL CORPORATION

Azusa, California

CONTENTS

CONTRACT FULFILLMENT STATEMENT

This quarterly report is submitted in partial fulfillment of Contract N7onr-462, Task Order III, and covers the work done from 1 September through 30 November 1953.

I. KINETIC STUDY OF THE THERMAL DECOMPOSITION OF NITROMETHANE

A. INTRODUCTION

1. The investigation of the thermal decomposition of nitromethane at relatively high pressures (200 psi) was continued. During this report period the effect on the decomposition reaction of additives that are known to lower the characteristic length and pressure requirements in nitromethane motors was determined. Certain tentative conclusions were reached which will have to be confirmed and extended. Work during this period was delayed because of difficulties with the mass spectrometer.

B. BACKGROUND AND EXPERIMENTAL RESULTS

1. The principal difficulty of using nitromethane as a monopropellant in conventional rocket motors is that relatively high chamber pressures and large values of characteristic length (L^*) must be employed in order to achieve stable combustion. However, when 5% or more oxygen is added to the system, the L^* and pressure requirements are considerably reduced. Another additive which has been found effective, although not to the same extent as oxygen, is chromium acetyl acetonate (CAA). Ethylene oxide alone and especially when mixed with chromium acetyl acetonate has also been shown to improve the combustion stability of nitromethane in rocket motors (References 1, 2).

2. Experiments carried out during this investigation (Reference 3) have shown that in the presence of oxygen the rate of decomposition of nitromethane at 355°C is not significantly affected, but that important intermediate products such as hydrogen cyanide, acetonitrile, and propionitrile are almost completely eliminated. Since these compounds are endothermic and are formed in relatively large quantities, it was concluded that oxygen added to nitromethane in a rocket motor eliminates the cyanides, thus increasing the heat available during intermediate stages of the decomposition. In the presence of oxygen there appears to be some increase in the formation of nitric oxide and nitrogen dioxide, which are also endothermic compounds; there is, however, an overall increase in the heat liberated.

a. During this report period three phases of the action of additives were studied:

(1) The effect of time and temperature on the concentration of the intermediate compounds and on the heat liberated.

(2) The effect of initial pressure of nitromethane on the concentration of intermediate compounds.

(3) The effect of chromium acetyl acetonate and of ethylene oxide on the rate of decomposition and on the products of the decomposition of nitromethane.

b. Previously the decomposition products were determined after 2,5,15, and 30 minutes reaction time at 355°C (Reference 3). In order to include data on experiments in which all the nitromethane had decomposed, tests were carried out after 24 and 30.5 hours of reaction time (Table I). The results indicate that the concentration of hydrogen cyanide decreases with time, whereas that of acetonitrile increases. As a consequence, the total fraction of the cyanides decreases less rapidly than the fraction of hydrogen cyanide alone. The concentration of nitric oxide, another endothermic compound, decreases considerably with time, and that of carbon dioxide, a highly exothermic compound, increases. This shift in products in favor of more exothermic compounds causes the heat released per mole of decomposing nitromethane to increase with time (Table II). It should be noted that the effect of the endothermicity of the cyanides is less significant in the later stages of the reaction, not only because these substances decrease somewhat in percentage (and shift to the less endothermic acetonitrile) but also because highly exothermic compounds such as carbon dioxide represent a larger portion of the reaction products. Since carbon dioxide has a heat of formation of +94 kcal, and hydrogen cyanide -31 kcal an increase of one mole of carbon dioxide would cancel the negative heat effect of three moles of hydrogen cyanide.

c. Two tests were made at 404°C, for 1.3 and 1.6 hours (Table III). It is seen that the product distributions are similar to those of the long-duration runs at 355°C. The heats of reaction are shown in Table IV.

d. Table I also includes the products obtained from tests at two different initial pressures (Runs 171 and 92). There does not appear to be a very large change in product distribution for a 3.5 times pressure variation; however, the shift in products that did occur caused a 24% increase in the heat liberated. The greater exothermicity of the reaction at the higher initial pressure may be significant, but further tests will have to be made to confirm it.

e. The products obtained from a test with added ethylene oxide and one with an added mixture of ethylene oxide and chromium acetyl acetonate are shown in Table V. A third test was made with added chromium acetyl acetonate alone, but the results are somewhat uncertain because of operational difficulties with the mass spectrometer. This test will be repeated, and will be discussed in a subsequent report. The results show that in the presence of these additives, hydrogen cyanide is reduced in quantity and propionitrile is eliminated.* The effect on acetonitrile is somewhat uncertain, since the amount of this compound seems to increase in the presence of the additives. The total fraction of cyanides, however, appears to be lowered, although not to the same extent as with added oxygen, when they are completely eliminated. The amount of nitric oxide, another endothermic intermediate, is lowered substantially in the presence of (1) ethylene oxide and (2) ethylene oxide plus chromium acetyl acetonate. On the other hand, the additives appear to bring about a significant increase in the amount of carbon

* In Run 170 (ethylene oxide + CAA) some evidence was found for the formation of β-hydroxypropionitrile.

dioxide, a highly exothermic compound. All these shifts in product distribution cause an increase in the heat liberated, and are more pronounced with a mixture of ethylene oxide and chromium acetyl acetonate than with ethylene oxide alone (Table V).

f. Polarographic analyses were made to determine the amount of nitromethane decomposed in the presence and absence of chromium acetyl acetonate. The data indicate that there may be an increase in decomposition with added chromium acetyl acetonate; however, the reproducibility of the data was not as good as had been obtained previously. Work is being done to clarify this matter, and the results will be discussed in a subsequent report.

C. DISCUSSION

1. Crocco and others (Reference 4) have developed theories relating unstable combustion to the fact that the processes responsible for the transformation of the propellants into high-temperature gases require a certain time. He considers the time delay mainly the result of physical processes such as atomization, vaporization, and heating of liquids and gases. The chemical reactions are assumed to take place in a very short time near the end of the time lag, the latter comprising the time between injection and the point when sudden transformation into hot gases at the final temperature occurs. It is further assumed in Crocco's theory of unstable combustion that the chamber pressure is oscillating and that the time lag and the chamber pressure are in a relationship such as the following:

$$\int_{t-\tau}^{t} p^n \, dt = \text{constant}$$

where

p = chamber pressure

t = time when deflagration temperature is reached

n = constant

τ = time lag

If the pressure is oscillating the time lag will also be oscillating; this in turn will cause the burning rate to oscillate. If the oscillations of the burning rate and of the pressure are in phase, self-excited oscillations may exist and give rise to unstable combustion. This will occur if the average time lag and the pressure oscillations meet certain relationships.

2. Crocco considers the time necessary to convert nitromethane to the final products very short compared with the time required for heating nitromethane to the deflagration temperature. In the present investigation, some evidence has been found that in addition to the delay due to physical process there may also be an appreciable chemical delay associated with reaction (2) of the following sequence:

$$\text{Nitromethane} \longrightarrow \text{Intermediates} \qquad (1)$$

$$\text{Intermediates} \longrightarrow \text{Final Products} \qquad (2)$$

It appears that an important function of the additives such as oxygen, chromium acetyl acetonate, and ethylene oxide may be to increase the evolution of heat in the early stages of the reaction by causing more exothermic products to be formed. A particular additive may be responsible for the elimination of certain intermediates only, but the effect in all cases would be an increase in the available heat. It should be pointed out that an additive that increases the rate of decomposition of nitromethane will of course lower the temperature at which reaction (1) becomes appreciable, and thus shorten the physical delay time. Further tests will have to be conducted to assess the relative contribution of an additive to the acceleration of the decomposition of nitromethane itself and to the transformation of the intermediates to final products.

II. RESEARCH ON THE PREPARATION OF NEW ROCKET PROPELLANTS

A. INTRODUCTION

The oxidation of trimethylhydrazine with yellow mercuric oxide and the reaction of trimethylhydrazine with formaldehyde have been further investigated. Attempts have been made to reduce methylene unsym.-dimethylhydrazine, $(CH_3)_2NN = CH_2$, to trimethylhydrazine catalytically, since the latter compound serves as the starting material in these reactions.

B. THE OXIDATION OF TRIMETHYLHYDRAZINE WITH MERCURIC OXIDE

The attempted oxidation of trimethylhydrazine to hexamethyltetrazane with yellow mercuric oxide in boiling diethyl ether has been carried out on a larger scale than previously reported. It was found that the filtered ether solution contained only about 25 per cent of the original reducing function, and that when the ether was removed, a dark-red oil remained. Distillation afforded a 5 weight per cent yield (based on trimethylhydrazine) of a red oil, b_{10} 50°C, which could not be characterized. Additional experiments are planned in which the oxidation will be conducted under milder conditions, since apparently any hexamethyltetrazane formed in the above experiment was oxidized further.

C. THE REACTION OF TRIMETHYLHYDRAZINE WITH FORMALDEHYDE

The reaction of aqueous formaldehyde with trimethylhydrazine was carried out by the dropwise addition of 5 g of formalin (0.067 mole of HCHO) to well-stirred trimethylhydrazine (0.134 moles) at 25 to 35°C. The product was then salted out at 25 to 35°C with sodium hydroxide or sodium carbonate. If the trimethylhydrazine was maintained at 10°C during the addition, no product could be salted out. The product was dried over solid sodium hydroxide and distilled. Approximately half the trimethylhydrazine was recovered; the residual oil (4 g) was colorless, b_{20} 80°C, $n_D^{25°}$ 1.4387. Addition of ethereal picric acid to an ethereal solution of the oil gave only trimethylhydrazine picrate. These facts suggest that initially the following reaction occurred,

$$(CH_3)_2NNHCH_3 + HCHO \longrightarrow (CH_3)_2NN(CH_3)CH_2OH$$

but that the reaction is apparently reversible in ethereal picric acid solution. Work is now in progress to determine whether the methylol compound will react with additional trimethylhydrazine under more drastic conditions:

$$(CH_3)_2NN(CH_3)CH_2OH + (CH_3)_2NNHCH_3 \longrightarrow \left[(CH_3)_2NN(CH_3)\right]_2CH_2 + H_2O$$

Reaction of the methylol with other alkyl hydrazines will be investigated, although the reversibility of the trimethylhydrazine-formaldehyde reaction may prevent the isolation of new products because of side reactions:

$$(CH_3)_2NN(CH_3)CH_2OH \longrightarrow (CH_3)_2NNHCH_3 + HCHO$$

$$HCHO + (CH_3)_2NNH_2 \longrightarrow (CH_3)_2NN = CH_2 + H_2O$$

D. THE REACTION OF HYDRAZINE HYDROCHLORIDE WITH PARAFORMALDEHYDE

Because of the known reaction of ammonium chloride and paraformaldehyde to yield trimethylamine in good yield (Ref. 5), the analogous reaction of hydrazine hydrochloride and paraformaldehyde was briefly investigated to determine whether alkylation of hydrazine could be achieved by this method. An intimate mixture was made of 25 g of paraformaldehyde and 20 g of hydrazine dihydrochloride, and this was then slowly heated in a flask equipped with a reflux condenser. At 55°C the solid suddenly turned liquid, evolving gas and becoming dark brown. After this vigorous reaction subsided, the liquid was

heated to 150°C for 1 hr. The reaction mixture (liquid at room temperature) did not reduce acidic potassium iodate, and when potassium hydroxide was added, a dark-brown solid formed. This solid, soluble in water and ethanol and insoluble in ether, could not be successfully purified by crystallization. Possibly instead of reacting by an alkylation process such as

$$3(CH_2O)_x + N_2H_4 \cdot 2HCl \longrightarrow (CH_3)_2NNH_2 + CO_2 + H_2O + 2HCl$$

the product is the trimer of formaldehyde hydrazone reportedly formed from hydrazine hydrate and formalin (Ref. 6). The vigorous reaction and evolution of gas make it appear that reactions other than this also occur, at least to some extent.

E. THE CATALYTIC REDUCTION OF METHYLENE-UNSYM.-DIMETHYLHYDRAZINE

1. Attempts have been made to reduce methylene-unsym.-dimethylhydrazine to trimethylhydrazine catalytically, since the only known method for preparing the latter compound involves a tedious and expensive reduction with lithium aluminum hydride (Ref. 7). Hydrogenations of the methylene compound were carried out with a 10 per cent palladium-on-charcoal catalyst at 1 atm and ambient temperature.

2. When water was used as the solvent exactly one mole of hydrogen was absorbed, and an 85 per cent yield of dimethylhydrazine (isolated as the picrate) was obtained. This reaction product apparently results from the hydrolysis of the methylene compound and subsequent reduction of formaldehyde:

$$(CH_3)_2NN = CH_2 + H_2O \longrightarrow (CH_3)_2NNH_2 + HCHO$$

$$HCHO \xrightarrow{2(H)} CH_3OH$$

3. When n-butyl ether was used as the solvent approximately 0.5 mole of hydrogen was absorbed. Only unreduced starting material was recovered. Presumably resinification occurred to some extent on the catalyst.

4. When absolute ethanol was used as the solvent exactly one mole of hydrogen was absorbed. Two reaction products were obtained, but these have not yet been identified. The first of these precipitated when ether was added to the ethanol solution (after removal of the catalyst). This material is a white crystalline solid melting at higher than 300°C; it is soluble in water to give a neutral solution; it is insoluble in ether; and its acid solution does not reduce iodate. The second compound was isolated as the picrate by the addition of ethereal picric acid to the filtrate from the first precipitation. Purification of the picrate is now in progress.

5. In connection with further attempts to reduce methylene-unsym.-dimethylhydrazine, chemical (i.e., non-catalytic) reductants such as zinc--ammonium acetate will also be used.

III. STUDY OF THE FEASIBILITY OF EMPLOYING ACETYLIDE SALTS AS PROPELLANT COMPONENTS

A. In the consideration of various compounds for possible use as additives to liquid fuels, the use of acetylide salts was suggested. The ionic nature of the compounds, and the energy of the triple bond are factors which would make them advantageous both as freezing-point depressants and as high-energy fuels. Metathetical reactions of the type

$$BX + M(C\equiv CH) \longrightarrow B(C\equiv CH) + MX$$

where B is a nitrogen-containing cation, X is a suitable anion such as a halide, and M is a metal ion such as sodium, were considered for synthesis of these compounds. Initial investigation indicated that guanidine acetylide could not be prepared, because of the weakly basic nature of guanidine. The preparation and isolation of tetramethyl ammonium acetylide is being studied at the present time.

B. The extreme solubility of sodium nitrate in liquid ammonia suggested a method for preparing tetramethyl ammonium acetylide. In this method, sodium nitrate would be extracted from a mixture of sodium acetylide and tetramethyl ammonium nitrate, using liquid ammonia in a Soxhlet extractor. In the reaction

$$(CH_3)_4NNO_3 + NaC\equiv CH \rightleftharpoons NaNO_3 + (CH_3)_4NC\equiv CH$$

the removal of the sodium nitrate would force the reaction to the right, while the relatively insoluble tetramethyl ammonium acetylide would concentrate in the thimble.

1. The extraction was carried on for a period of 8 hours using a mixture of sodium acetylide and tetramethyl ammonium nitrate in a mole ratio of 17:1. The large excess of sodium acetylide was used in order to ensure the presence of sufficient reagent throughout the extraction; its solubility is approximately 30 times greater than that of tetramethyl ammonium nitrate. Intermittent tests of the thimble residue served to determine when all the nitrate ion had been removed. When diphenylamine in concentrated sulfuric acid gave a negative test for nitrate ion, the thimble residue was analyzed for nitrogen by the Kjeldahl method; a portion of the residue was also treated with water and then titrated with standard acid for total alkalinity. The absence of nitrate ion permitted a separate calculation of the distribution of sodium acetylide and tetramethyl ammonium acetylide, based first on the acid-base titration, then on the nitrogen determination. The results were as follows:

	Acid-Base Analysis	Kjeldahl Nitrogen Analysis
$NaC\equiv CH$	96%	94%
$(CH_3)_4NC\equiv CH$	4%	6%

2. This experiment was repeated with similar results, indicating the presence of tetramethyl ammonium acetylide. The loss of unreacted tetramethyl ammonium nitrate and tetramethyl ammonium acetylide by direct solution during extraction could not be determined. Probably the solubility of tetramethyl ammonium acetylide is high enough that the time required for complete removal of nitrate ion also allowed removal of a considerable portion of the desired acetylide salt. Extraction of other salts was tried in a similar manner in an effort to produce a residue richer in tetramethyl ammonium acetylide.

C. Extraction of a mixture of tetramethyl ammonium iodide and sodium acetylide (10/1 molar ratio $NaC\equiv CH/(CH_3)_4NI$), produced a residue that contained 78% tetramethyl ammonium iodide and 22% sodium acetylide; none of the desired product was found. A weight loss of 70.3% from the original mixture was observed in 2-1/4 hr, 84.3% of which was sodium acetylide and 15.7% tetramethyl ammonium iodide.

D. Soxhlet extraction of a mixture of tetramethyl ammonium chloride and sodium acetylide produced a residue that contained 17% tetramethyl ammonium acetylide, 45% tetramethyl ammonium chloride, and 35% sodium acetylide. A weight loss of 70% from the original mixture (2:1 molar-ratio $NaC\equiv CH/(CH_3)_4NCl$) in 1/2 hr included approximately 50% of the tetramethyl ammonium ion originally present, a serious disadvantage to the use of this method for the synthesis of tetramethyl ammonium acetylide.

E. Indications that tetramethyl ammonium acetylide is appreciably less soluble in liquid ammonia than tetramethyl ammonium chloride suggested the possibility of direct precipitation from a saturated solution of the chloride by the addition of sufficient sodium acetylide solution. An experiment carried out in this manner at -30°C produced a light, flocculent precipitate. After a preliminary observation, the experiment was repeated on a larger scale to furnish sufficient quantity of precipitate for analysis. A 5.2-g quantity of tetramethyl ammonium chloride was dissolved in 650 ml of anhydrous ammonia to produce a saturated solution at -30°C. A solution of 2.4 g of sodium acetylide in 75 ml of ammonia was added and the light, fluffy precipitate was obtained. In attempting to increase the quantity of precipitate by evaporation of the solvent, it was found impossible to prevent the precipitation of the salts on the sides of the Dewar flask in their original proportions. Work is planned to eliminate this problem.

F. The extreme insolubility of sodium fluoride in liquid ammonia offers a possible driving force for the metathesis from tetramethyl ammonium fluoride and sodium acetylide. An initial preparation of tetramethyl ammonium fluoride was carried out in the following manner:

$$2(CH_3)_4NCl + Ag_2O + H_2O \longrightarrow 2AgCl + 2(CH_3)_4NOH$$

$$(CH_3)_4NOH + HF \longrightarrow (CH_3)_4NF + H_2O$$

An excess of hydrofluoric acid produced the acid salt having the formula $(CH_3)_4NF \cdot 2HF$. This salt was recrystalized from H_2O-EtOH solution. The solubility of $(CH_3)_4NF \cdot 2HF$ in liquid ammonia at -30°C was determined as 0.00062 mole per 100 ml of solution. The normal salt is being prepared at the present time.

G. The possibility was considered of preparing tetramethyl ammonium acetylide from tetramethyl ammonium radical (in the form of its mercury amalgam) by proper addition of acetylene. Preliminary investigation was carried out using the analogous system of a sodium-mercury amalgam to produce sodium acetyli Acetylene was bubbled through a 0.5% sodium amalgam using ether as a covering solution to prevent oxidation. No evidence of sodium acetylide formation could be observed, however. Dimethylformamide was substituted as the covering liquid, since acetylene is extremely soluble in this material. Again no evidence of sodium acetylide formation could be observed. A 2% sodium amalgam was then used and the experiment was repeated. Little if any reaction was observed. Further experiments will be carried out in order to determine if it is feasible to produ tetramethyl ammonium acetylide from the free radical.

IV. ENGINE TEST PROGRAM

A. PERFORMANCE EVALUATION OF THE PENTABORANE AND LIQUID FLUORINE PROPELLANT SYSTEM

Engine testing of the pentaborane and liquid fluorine combination has been suspended pending the availability of test facilities that will eliminate the present hazards to personnel resulting from inadequate ventilation of the test bay.

B. PERFORMANCE EVALUATION OF THE UNSYM.-DIMETHYLHYDRAZINE AND LIQUID OXYGEN PROPELLANT SYSTEM

1. After several malfunctions using liquid oxygen directly in the coil used normally for liquid fluorine, the system has been simplified so that the oxygen may be injected directly into the thrust chamber from the oxidizer cylinder. This simpler system, which does not require the use of the hand-operated Kerotest valves necessary for handling fluorine, will allow the tests to be conducted in a more rapid manner than would otherwise be possible. The first performance tests are scheduled for the first week of the next report period.

2. An injector with impinging streams axial to the wall of the chamber over the entire mixture-ratio range is being employed in this test series. The design features of this injector will be included in the next report, when results of its efficiency become available.

REFERENCES

1. Research Technical Memorandum No. 63, Aerojet Engineering Corp., 16 June 1950 (Confidential).

2. Aerojet Report No. 741, 17 September 1953 (Restricted).

3. Aerojet Report No. 747, 8 October 1953 (Confidential).

4. L. Crocco, J. Am. Rocket Soc. 21, 163 (1951).

5. R. Adams and C. S. Marvel, Organic Synthesis, Vol. I, p. 531, John Wiley and Sons, N.Y., 1946.

6. R. Stolle, Ber. 40, 1505 (1907).

7. J. B. Class et al., J. Am. Chem. Soc. 75, 2937 (1953).

TABLE I

PRODUCTS OF THE DECOMPOSITION OF NITROMETHANE

EFFECT OF DURATION OF TEST AND OF INITIAL PRESSURE*

Temperature: 355°C

$$\frac{\text{moles product}}{\text{moles nitromethane decomp.}} \times 100$$

Product	Run 138 179 psia	Run 96 234 psia	Run 119 259 psia	Run 92 310 psia	Run 171 89 psia	Run 168 234 psia	Run 169 231 psia
C_2H_5CN	4.4	2.1	1.5	---	---	---	---
CH_3CN	5.1	0.8	2.0	4.1	3.7	9.3	13.2
HCN	35.4	36.5	54.4	43.5	38.7	22.2	17.8
N_2O	2.0	1.31	0.2	2.8	2.1	---	---
NO	41.9	46.6	38.8	26.3	34.7	1.7	1.9
N_2	4.3	5.5	5.4	10.5	9.0	35.4	33.2
CO_2	8.4	9.9	18.5	31.4	27.3	33.7	37.2
CO	17.3	20.5	8.7	12.2	17.1	19.5	14.1
CH_4	9.3	12.7	5.0	4.8	9.5	6.1	4.6
H_2O	101.4	99.6	105.2	105.9	91.0	110.9	109.8
CH_2O	6.2	2.6	5.0	---	---	---	---
Duration	2 min	5 min	15 min	31 min	31 min	24 hr	30.5 hr

* A portion of this information was contained in Table VI of Ref. 3. Two of the values reported there were in error; and were corrected for this table.

TABLE II

THERMAL DECOMPOSITION OF NITROMETHANE

HEAT LIBERATION*

Temperature: 355 and 404°C

Run	Pressure psia	Temp. °C	Duration	Heat Liberated kcal
138	179	355	2 min	31.4
96	234	355	5 min.	32.2
119	259	355	15 min	35.6
171	89	355	31 min	42.6
92	310	355	31 min	52.2
168	234	355	24 hr	71.7
169	231	355	30.5 hr	73.2
172	235	404	1.3 hr	64.9
174	242	404	1.5 hr	55.0**

* Both reactant and products are considered to be at ambient temperature.

** This value may be in error because of the low conc. of water (see Table III).

TABLE III

PRODUCTS OF THE DECOMPOSITION OF NITROMETHANE

Temperature: 404°C

$$\frac{\text{moles product}}{\text{moles Nitromethane decomp}} \times 100$$

Product	Run 172 235 psia	Run 174 242 psia
CH_3CN	9.2	9.4
HCN	22.9	22.4
NO	6.6	6.2
CO_2	33.0	33.7
H_2O	102.5	84.3*
CH_4	7.9	7.2
N_2	28.3	26.9
CO	18.0	17.7
Duration	1.3 hr	1.5 hr

* There is evidence that this value is in error and should be somewhat higher.

TABLE IV

THERMAL DECOMPOSITION OF NITROMETHANE
EFFECT OF ADDITIVES ON THE HEAT OF REACTION*

Temperature: 355°C

Run	Initial Pressure psia	Duration, min.	Additive	Heat Evolved kcal per mol
96	234	5	---	32.2
158	184	5	24.7% Ethylene Oxide	50.2
170	253	5	19.9% Ethylene Oxide Plus 2% CAA**	67.4

* Both reactant and products are considered to be at ambient temperature.

** Chromium acetyl acetonate.

TABLE V

THERMAL DECOMPOSITION OF NITROMETHANE

EFFECT OF ADDITIVES ON PRODUCT DISTRIBUTION

Temperature: 355°C
Duration: 5 min

$$\frac{\text{moles product}}{\text{moles nitromethane decomp.}} \times 100$$

Product	Run 96 234 psia	Run 158 184 psia	Run 170 253 psia
C_3H_5CN	2.1	---	---
C_3H_5NO	---	---	1.4
CH_3CN	0.8	1.0	3.6
HCN	36.5	32.7	23.0
N_2O	1.31	---	---
NO	46.6	28.1	9.6
N_2	5.5	19.1	31.2*
CO_2	9.9	24.9	40.1
CO	20.5	27.1	19.4
CH_4	12.7	13.3	6.0
H_2O	99.6	94.9	94.6
CH_2O	2.6	---	---
Additive	---	24.7% Ethylene Oxide	2% CAA** 19.6% Ethylene Oxide

* This value may be too high.

** Chromium acetyl acetonate.